Support information:

Mechanism of the Stoddart-Heath bistable rotaxane molecular switch

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Abstract

The supporting information is organized as follows:

- Section 1 describes the real device and our strategy to make a minimum structure device for quantum mechanics and device simulations.
- Section 2 describes the Green's Function method and procedures we use to calculate the electronic properties of the device structure described in section 1.
- Section 3 shows additional detailed results from the calculations.

Section 1 Device structures and our approximation

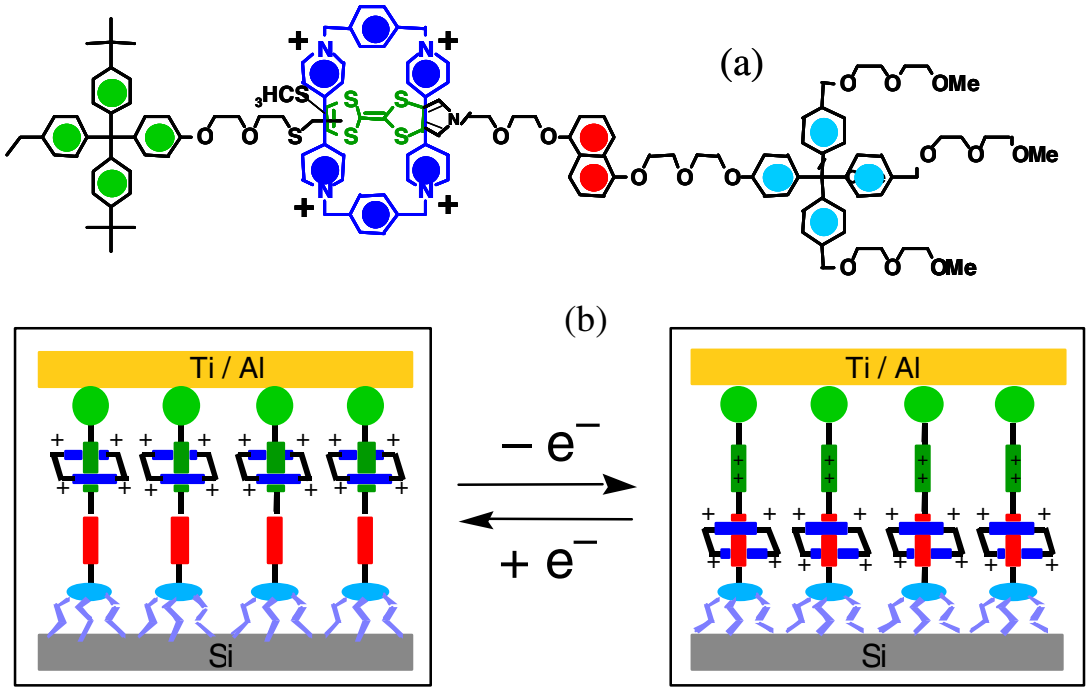

Figure 1. The Heath-Stoddart rotaxane switch

Figure 1 shows a schematic for the Heath-Stoddart rotaxane switch. The structure of the whole molecule is shown in Figure 1a. The backbone of molecules consists of four groups;

- left green; stopper to keep ring from coming off the backbone,
- TTF group green,
- napthyl group red, and
- right blue: stopper.

The ring component can be caused to shift between the TTF and napthyl group but cannot move off the backbone because of the left and right stoppers. Figure 1b shows the device structure, with the four components shown as colored boxes. The rotaxane was deposited on the poly-silicon surface and is expected to form a self-assembled monolayer. The second electrode, Ti/Al was deposited on the top of the monolayer.

We simplified the system as shown in Fig. 2 to make the DFT calculations practical, while maintaining the essence of the rotaxane switch. From original molecule (a), we cut off the right and left stoppers and neutralize the molecule with hydrogen atoms. Then we used the Dreiding force field [15] to optimize the geometry for three structures:

- ring over the TTF,
- ring over the napthyl, and
- ring over the linker in between

In all cases the four PF_6^- counterions are included. These structures were then reoptimized using AM1 [16] quantum mechanics, leading to the result that the ring-linker structure is higher than the other two. Next we deleted the hydrogen atom at the thiol and bond the thiol to a gold trimer at each end of the rotaxane. This Au_3 was included to provide an electrode for the I/V calculations. The Au_3 was constrained to lie in the plane perpendicular to the axis and 1.9 Å from the S. At the optimum AM1 geometry, we carried out DFT calculations (B3LYP) with the 6-31G basis on each atom except the Au atoms, where we used the Hay-Wadt core-valence effective core potential [12] (LACVP with 11 electrons per Au). We solved for the ground state Hamiltonian and orbitals for each state.[18]

To calculate the electrical conductivity, we used the Green's function formalism of Ratner and others [12-14], assuming that the coupling between the backbone of the rotaxane and the electrodes does not change as the ring moves. A DFT calculation at the B3LYP/LACVP level was performed at single point calculation to obtain the Fock Hamiltonian and Overlap matrices. These F and S matrices were then factored into electrode (Au_3) and molecule parts. In these calculations we choose the Fermi energy as –5.31eV, just as for bulk Au metal.

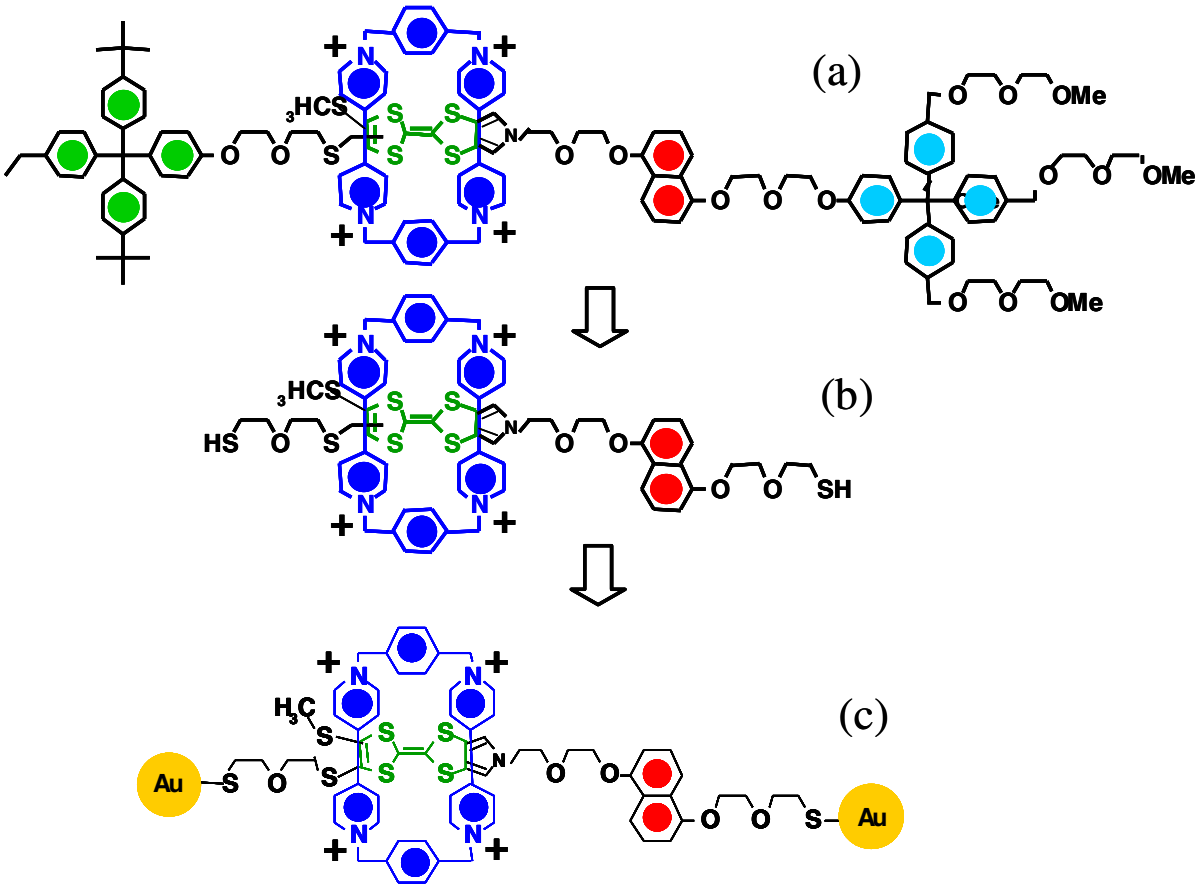

Figure 2. a) The rotaxane used in the experiments. b) The simplified rotaxane used in the calculations. c) The simplified rotaxane attached to a gold particle

Section 2. Implementation of Green's function theory for calculating I-V curves

Generally the current through molecules at is expressed as; [12-14]

$$I(V) = \frac{2e}{h}\int_{-\infty}^{\infty} T(E,V)[f_1(E,V_1) - f_2(E,V_2)]dE \qquad (1)$$

where f_i is the Fermi-Dirac function for a voltage Vi at electrode i(1 or 2). The transmission function, T(E,V), is the sum of transmission probabilities of all channels available at energy E and is obtained through the Green function of the molecule, G_M, as affected by the electrode contacts.

$$T(E,V) = Trace[\Gamma_1(V)G_M(E,V)\Gamma_2(V)G_M^+(E,V)] \qquad (2)$$

G_i describes the coupling at electrode i.

The Green function of the molecule in equation (2), G_M, is calculated from the molecular Hamiltonian, $H_{MM}(V)$, i.e.,

$$G(E) = \begin{bmatrix} g_1^{-1} & -\tau_1 & 0 \\ -\tau_1^+ & ES_{MM} - H_{MM} & -\tau_2^+ \\ 0 & -\tau_2 & g_2^{-1} \end{bmatrix} = \begin{bmatrix} G_1 & G_{1M} & G_{12} \\ G_{M1} & G_{MM} & G_{2M} \\ G_{21} & G_{M2} & G_2 \end{bmatrix} \qquad (3)$$

The submatrixes G and g represent Green functions when interactions among subsystems are included or excluded, respectively. g_i represents the electrodes and τ_i describe the metal-molecule coupling. H_{MM} and S_{MM} are the Fock and overlap matrices of the isolated molecule, respectively and E is the electron energy. Therefore, solving eq 3 for G_M, we obtain

$$G_M = [ES_{MM} - H_{MM} - \Sigma_1 - \Sigma_2]^{-1} \tag{4}$$

where

$$\Sigma_1 = \tau_1^+ g_1 \tau_1 \quad \text{and} \quad \Sigma_2 = \tau_2^+ g_2 \tau_2 \tag{5}$$

where S_i are the self-energy terms coupling between the molecule and the electrodes.

All the parameters needed can be obtained from the Fock and Overlap matrices based on DFT calculations.

$$F = \begin{bmatrix} H_{11} & H_{1M} & H_{12} \\ H_{M1} & H_{MM} & H_{M2} \\ H_{21} & H_{2M} & H_{22} \end{bmatrix} \quad \text{and} \quad S = \begin{bmatrix} S_{11} & S_{1M} & S_{12} \\ S_{M1} & S_{MM} & S_{M2} \\ S_{21} & S_{2M} & S_{22} \end{bmatrix} \tag{6}$$

The metal-molecule coupling term t_i can be determined by

$$\tau_1 = ES_{M1} - H_{M1} \quad \text{and} \quad \tau_2 = ES_{M2} - H_{M2} \tag{7}$$

H_{Mi} are the coupling matrix element between electrode and molecules.

The coupling G_i appearing in eq. 2 is given by

$$\Gamma_1 = i[\Sigma_1 - \Sigma_1^+] \quad \text{and} \quad \Gamma_2 = i[\Sigma_2 - \Sigma_2^+] \tag{8}$$

g_i are the surface green function of the electrode. For Au we approximate this as a diagonal matrix with each element proportional to their local density of states.

$$g_i = \begin{bmatrix} g_S & 0 & 0 & \ldots \\ 0 & g_p & 0 & .. \\ 0 & 0 & g_d & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{bmatrix} \tag{9}$$

Each orbital character s, p, d leads to different contributions, which we write as

$g_S = -0.0720\pi i$

$g_p = -0.0426\pi i$

$g_d = -0.1778\pi i$

based on reference 19,

To carry out these calculations we used the modified Huckel-IV2.0 code provided by Supriyo Datta's group based on above equations.

Section 3. Additional Calculational results

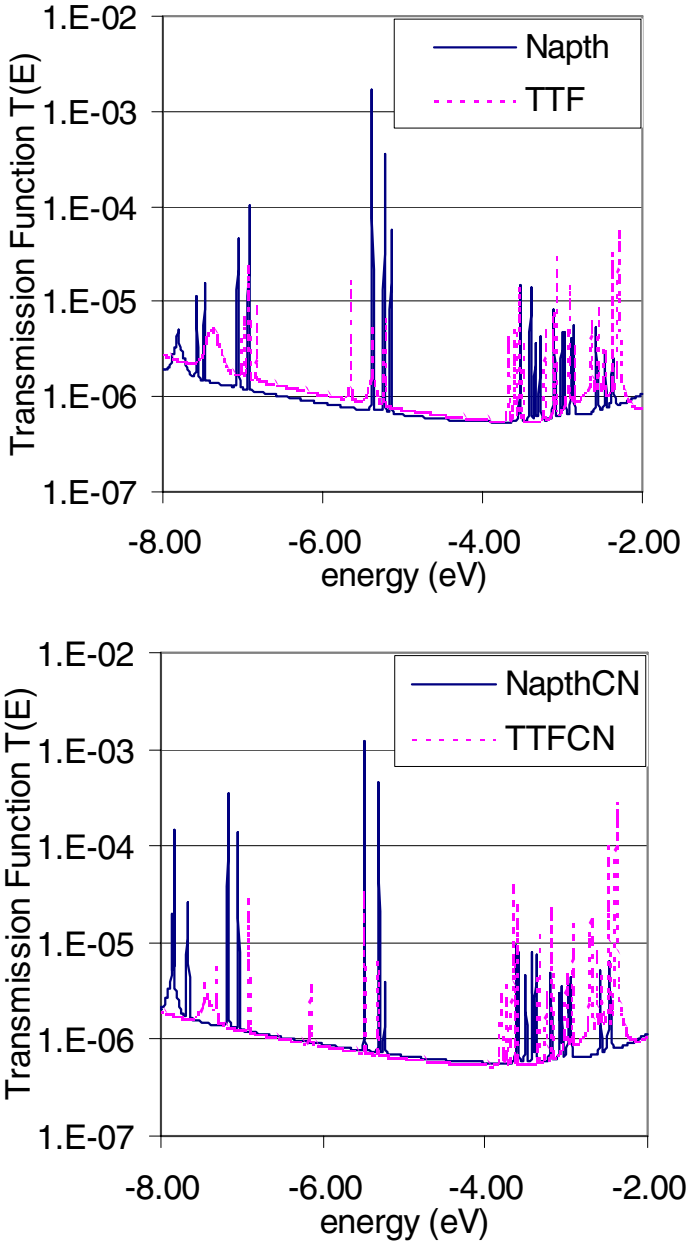

Figure 3. Transmission Function of roxataxane components.

Figure 3 shows the transmission function T(E) calculated from equation (2). The top figure compares rotaxane on the NAP group with rotaxane on the TTF group. Over the range between –6.0 to –4.0 eV, the ring on NAP leads to more than 100 times the transmission of ring on TTF. This is because the ring affects the characteristics of MOs.

The bottom figure compares rotaxane molecule on NAP-CN group with rotaxane on the TTF group.

Table 1. The calculated orbital energies (eV) of rotaxane components.

	NAP	TTF	NAPCN	TTFCN
HOMO-2	-5.89	-5.67	-5.86	-6.17
HOMO-1	-5.83	-5.60	-5.84	-6.00
HOMO	-5.38	-5.58	-5.49	-5.56
LUMO	-5.23	-5.38	-5.31	-5.51
LUMO+1	-5.15	-5.23	-5.24	-5.34
LUMO+2	-4.24	-4.97	-4.19	-4.22

Table 1 lists the frontier MOs of NAP, TTF, NAP-CN and TTF(CN) components. The characteristics of these MOs are shown in Figure 4, 5, 6 and 7 respectively. The characteristics of those MOs explains the mechanism of the molecular switch.

Figure 4, 5, 6, and 7 show the frontier MOs of NAP, TTF, NAPCN, and TTF(CN) respectively.

The HOMO, LUMO and LUMO+1 of NAP are all delocalized orbitals.

The HOMO, LUMO, LUMO+1 of TTF are localized molecular orbitals.

The HOMO and LUMO of NAP-CN are delocalized molecular orbitals. Notice that LUMO+1 becomes localized after CN addition. This MO contributes much lower transmission, as shown in Figure 9. LUMO and LUMO+1 are localized MOs. HOMO and HOMO-1 are localized at Au electrodes.

Figure 8 shows the I-V curves as discussed in the Text. The left I-V curve for NAP-CN shows two flat regions from contributions from two frontier MOs. The right I-V curve shows below 0.1 V NAP has a large slope comparing with the curve after 0.1 V, indicating that two different MOs contribute to this curve. Thus the modification by CN changes the ON/OFF ratio, even though the electronic conductivity does not change significantly. This means that the mechanism of the switch in conductivity is dominated by the shape of the MO instead of its MO energy level.

Figure 9 shows the transmission function of NAP, TTF, NAP-CN and TTF(CN) respectively. Each MO contributes a different transmission probability.

For rotaxane-NAP, the HOMO, LUMO and LUMO+1 are delocalized MOs and thus have $10^{-}2$ to 10^{-4} transmission probability.

However, the HOMO-2, LUMO and LUMO+1 of rotaxane-TTF only have ~10^{-5} transmission. The characteristic of the MOs in Figure 6 and Figure 7 clearly show the difference in localization of the MOs. The HOMO and HOMO-1 of rotaxane-TTF have small transmission probability because they are both localized Au orbitals. Similarly, the HOMO-1 of rotaxane-NAP leads to low transmission probability. The frontier orbitals of the CN modified rotaxane molecules are shown in Figure 3. We see that the LUMO+1 in NAP has become the LUMO in NAP-CN leading to increased delocalization. This leads to improved conductivity.

Figure 10 shows the electric conductivity of NAP, TTF, NAPCN and TTFCN respectively. The conductivities of TTF and TTF(CN) components range from 0.06 to 0.20 nA/V. In contrast, the conductivities of NAP and NAP-CN range from 1.00 to 9.0 nA/V. The peaks at around 0.2 V of NAP are dominated by the HOMO of NAP. The peaks at 0.0V and 0.40 V of NAP-CN conductivities are contributed from LUMO and HOMO of NAP-CN.

Figure 11 shows the density of states (DOS) of rotaxane molecules. The DOS identifies the position of each MO, but it does not indicate the shape characteristics of the MOs.

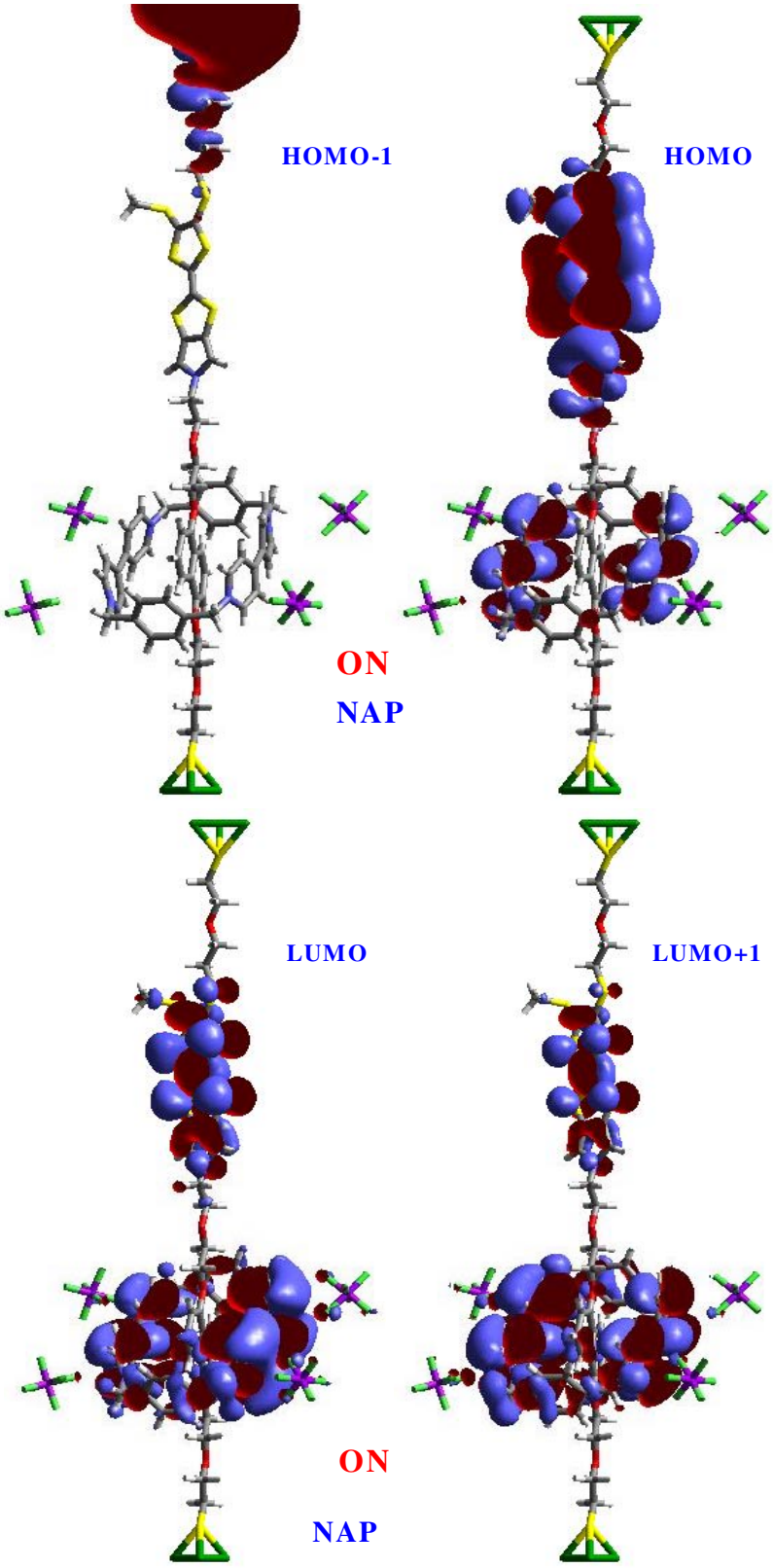

Figure 4. The characteristic MOs of rotaxane NAP.

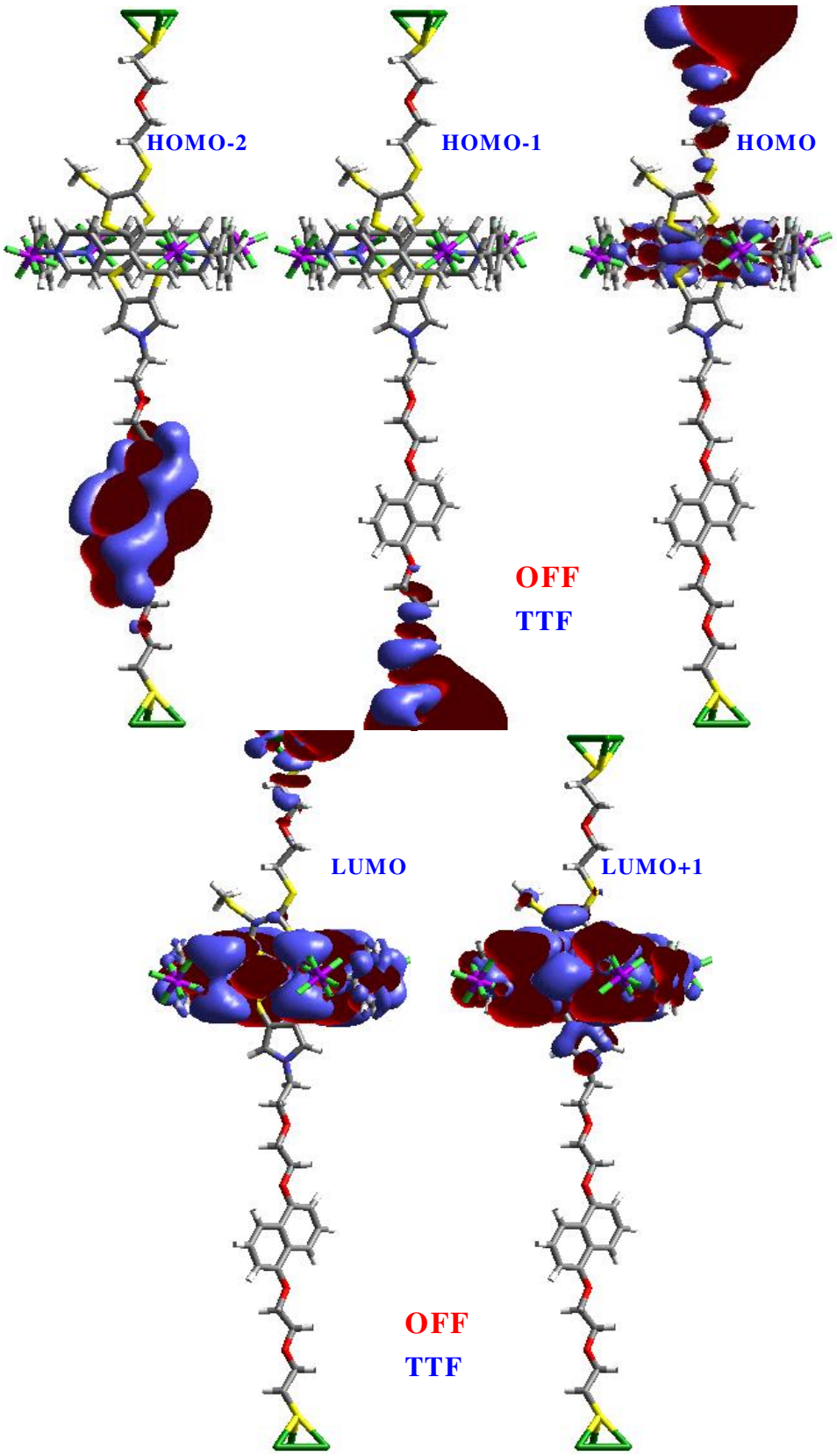

Figure 5. The characteristic MOs of rotaxane TTF.

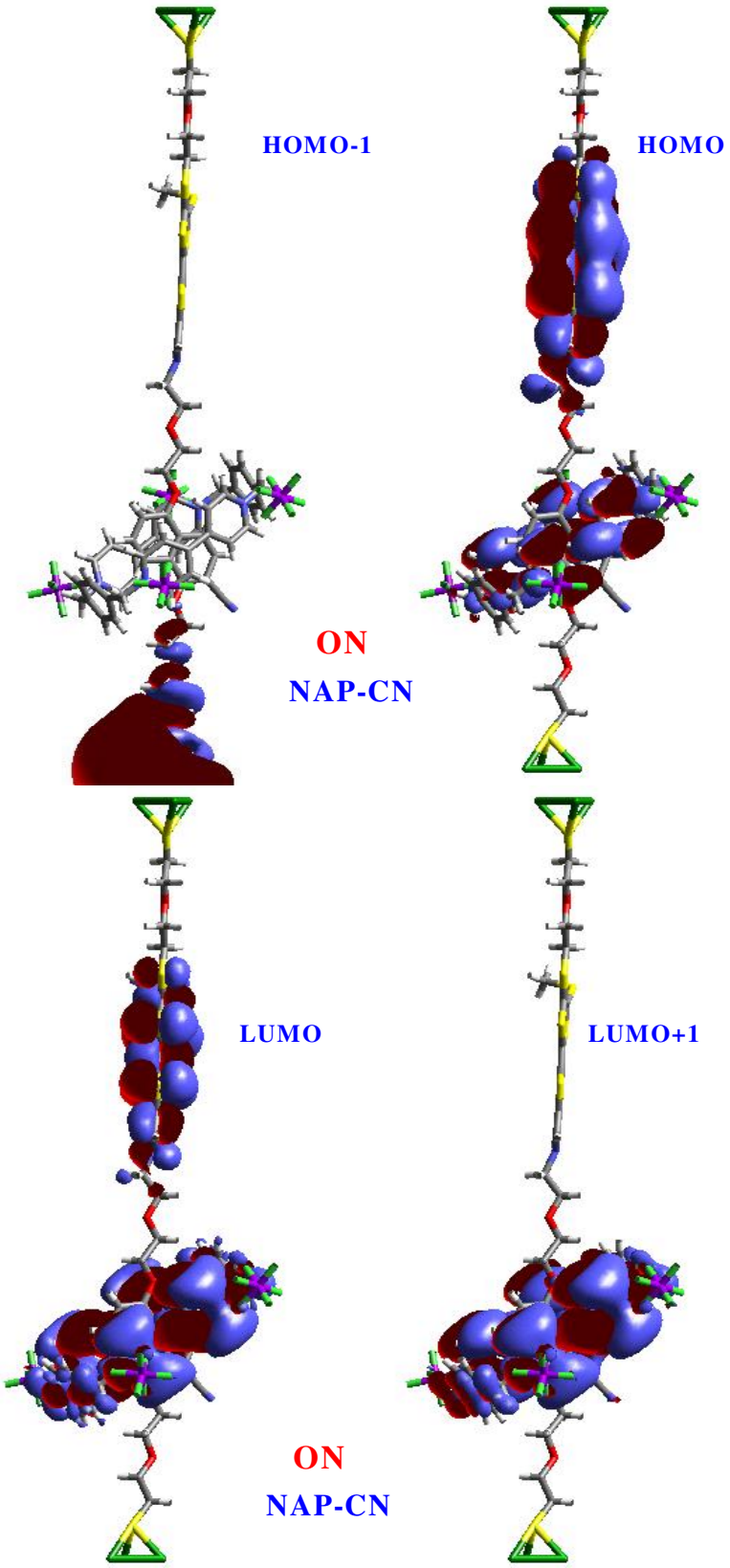

Figure 6. The characteristic MOs of rotaxane NAPCN.

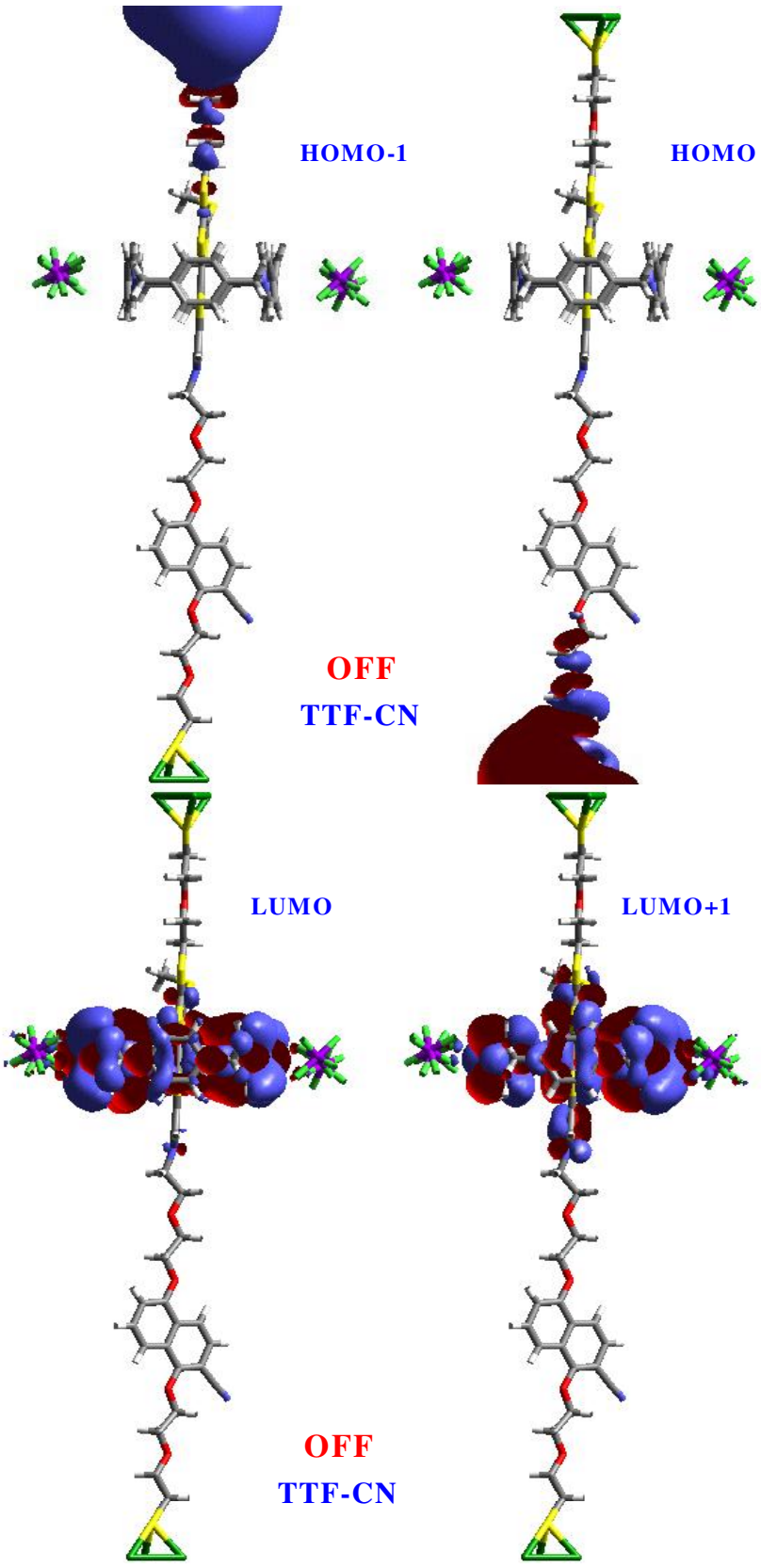

Figure 7. The characteristic MOs of rotaxane TTF-CN.

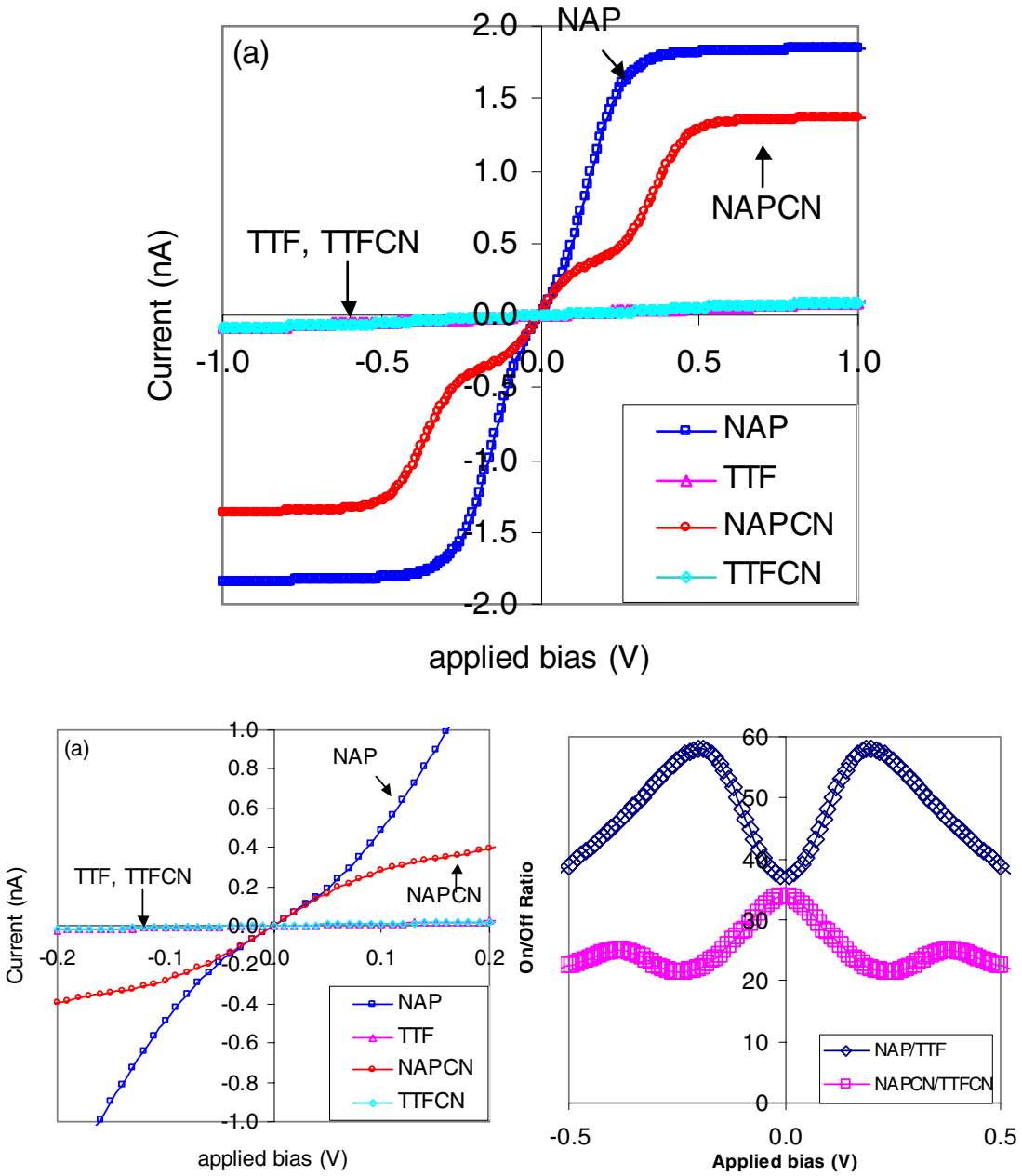

Figure 8. The I-V curves for various rotaxane systems. a). Scaling from 0-1 V bias. b) Scaling from 0-0.2 V bias. c) On/Off ratio of NAP/TTF and NAP-CN/TTF.

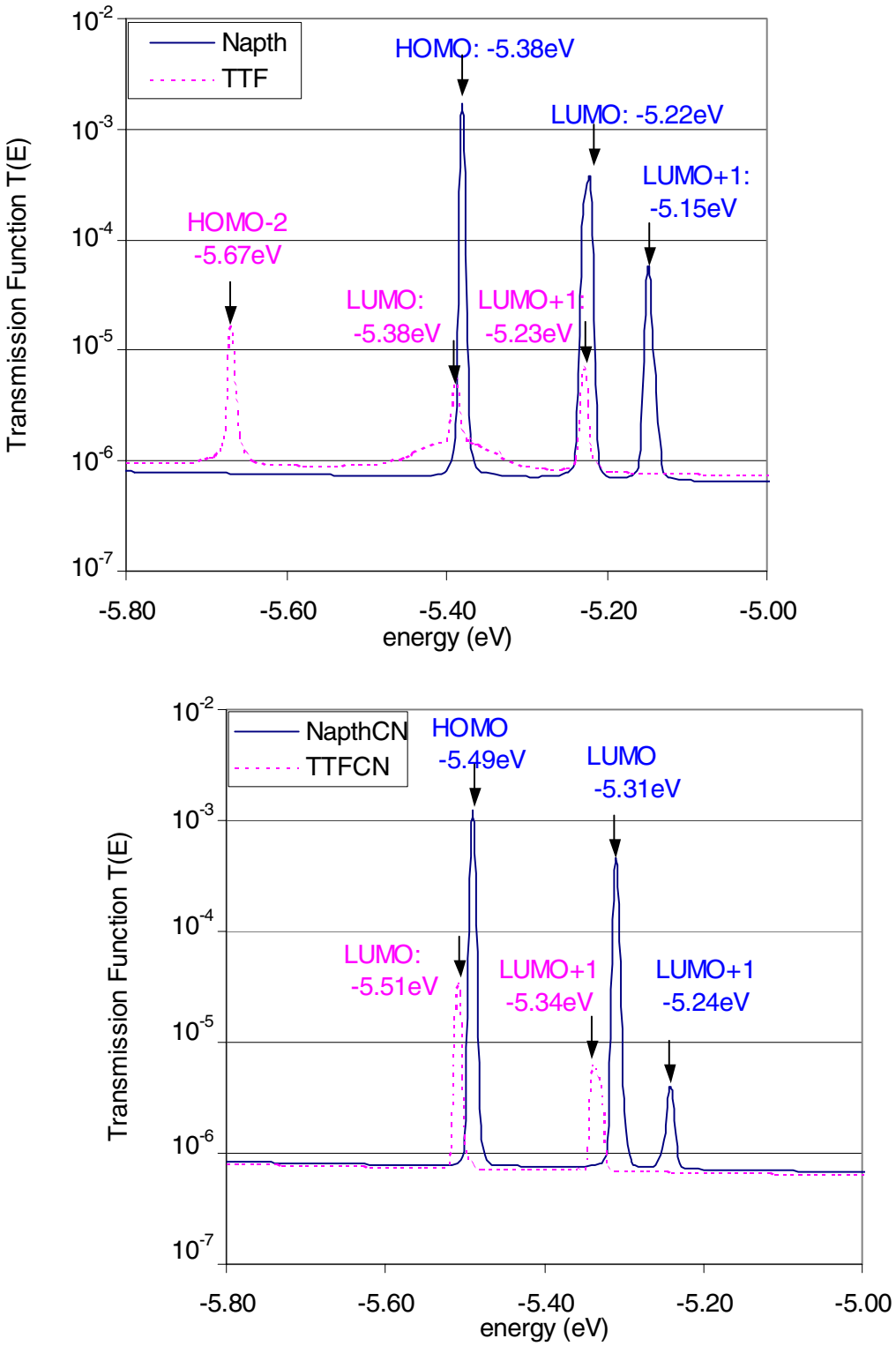

Figure 9. The contribution of each MO to the transmission function T(E).

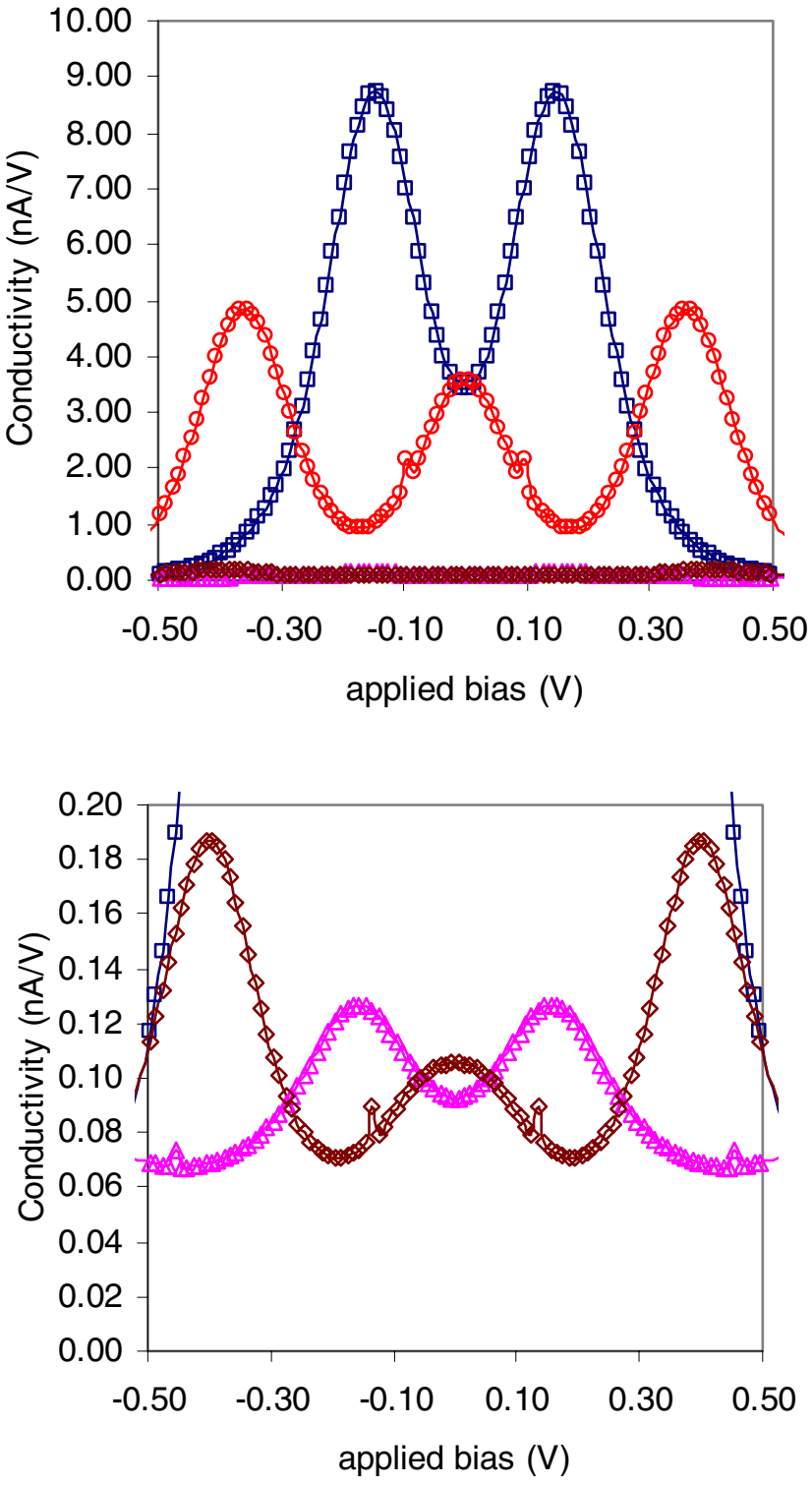

Figure 10. The conductivities of rotaxanes. Blue square is NAP, red circle is NAP-CN. Pink triangle is TTF and brown is TTF (for NAP-CN case).

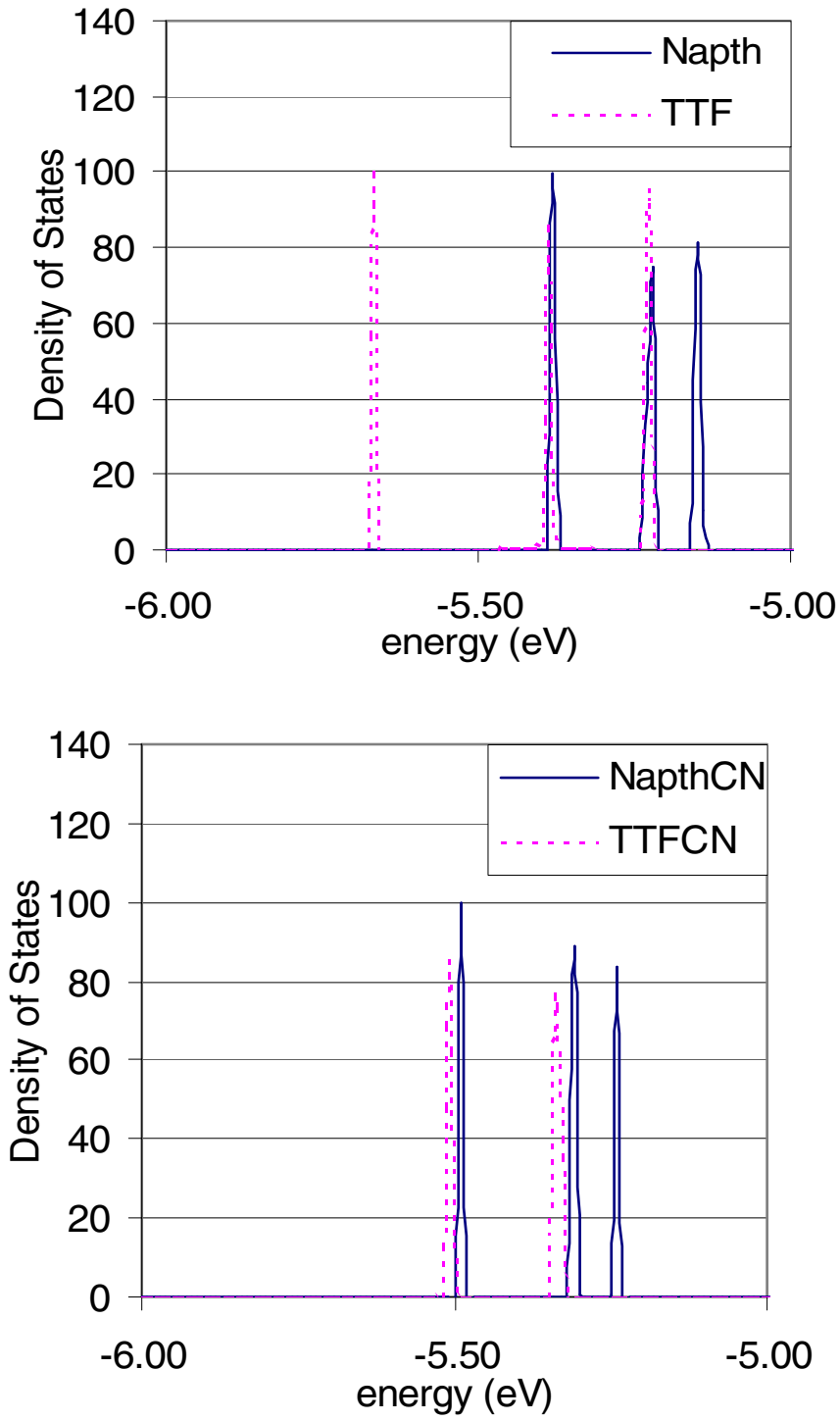

Figure 11. Density of State of rotaxane molecules.